

ANODIC DISSOLUTION OF NiS IN AMMONIA MEDIA

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ABSTRACT

The mountainous regions of Kazakhstan have the world's richest reserves of sulfide ores. Environmentally friendly sulphide recycling methods are extremely important for the economy of the future. In recent decades, hydrometallurgical methods for processing sulfides have been intensively developed. The latter is associated with the use of highly efficient technologies in new enterprises.

With an unusually large attention to the problem of processing sulfide materials from industrial production, the study of the electrochemistry of sulfides and the behavior of sulfides in various media received much less attention. Nevertheless, I. Ivanov's work on measuring potentials is noteworthy, showing that the potentials of nickel sulfides do not behave quite stationary, varying significantly over time, which indicates electrochemical processes on the surface of the sulfide. The article discusses the kinetics and electrochemical behavior of NiS in sulfite-ammonia, ammonia-dichromate and copper-ammonia electrolytes. Possible directions of NiS anodic dissolution's process course without passivation are considered. The results of the studies carried out simulating the behavior of sulfides in sulfate-sulfuric oxide and halogen-containing solutions, studies of the effect of cationic and anionic activators, changes in the surface of sulfides during dissolution, and methods for depassivation and acceleration of dissolution of sulfides were determined.

Key words: sulfide, anodic, NiS, dissolution, electrochemistry.

INTRODUCTION

Hydrometallurgical technologies for processing sulfide ores of non-ferrous metals are being intensively developed at modern enterprises [1-2]. It was previously established [3] that the presence of copper ions in autoclave leaching solutions has a significant catalytic effect on the dissolution of nickel sulfide. But the presence, both separately and together with copper of sulfate ions, is accompanied by passivation of the sulfide surface, which reduces the performance of the process (Fig. 1).

The aim of this work is to study the influence on the electrochemical behavior of nickel sulfide of the composition of the electrolyte and depassivating additives, such as NH_4OH and SO_3^{2-} , contributing to its active anodic dissolution.

Synthetic nickel sulfide — millerite (α NiS) was used as the object of study, since it was established [4] that upon oxidative dissolution of nickel sulfides Ni_3S_2 and Ni_7S_6 proceeding by the electrochemical mechanism [5], the surface is gradually enriched with higher sulfide, up to NiS [6]. Nickel sulfide NiS was synthesized according to a known method [7] from equimolar amounts of cathode nickel H0 and sulfur p.f.a. (pure for analysis) in an evacuated quartz ampoule. A working electrode was made by soldering a sample of nickel sulfide to a copper holder and insulating the non-working surface with nitrodope. Before the experiments,

the NiS surface under investigation (area 1 cm²) was cleaned with sandpaper No.0, washed with alcohol and distilled water. We used a glass cell GEC-2 (glass electrochemical cell) with an external thermostat UTU-2/77. Electrochemical studies were carried out on a PI-50-1.1 potentiostat with a PDP4-002 tablet potentiometer. We used a three-electrode circuit: the working electrode — the studied nickel sulfide, the auxiliary electrode — Pt, and the reference electrode — saturated silver chloride KCl, (AgCl/Ag). (The electrode potentials are given relative to a normal hydrogen electrode). CuSO₄·5H₂O c.p.(chemically pure), H₂SO₄ es.p. (especially pure), (CuOH)₂CO₃ p.f.a. (pure for analysis), K₂Cr₂O₇ c.p. (chemically pure), Na₂SO₃ (pure for analysis) were used to prepare electrolytes. The sweep speed of cyclic voltammograms (CVA) given in this article is 100 mV/s.

MATERIALS AND METHODS

1. Behavior of NiS in Na₂SO₄

The behavior of NiS in pure 1M Na₂SO₄ at 90°C is shown in (Fig. 1). As can be seen from the figure, at a potential of 100-150 mV, the NiS transitions to the passive state, up to 900-1000 mV.

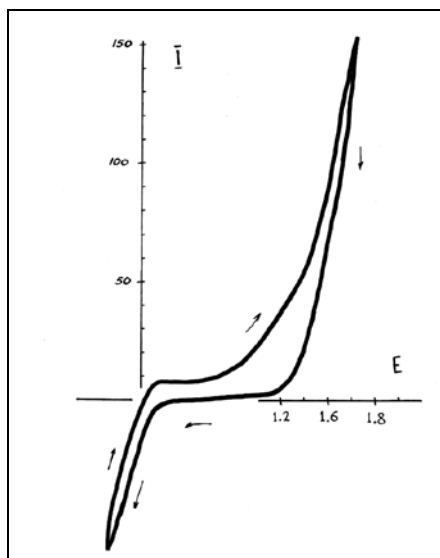


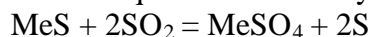
Fig.1. CVA NiS – at 90±0.5°C in 1M Na₂SO₄; pH = 2.2:

I – anode current, mA, E – electrode potential, V (n.h.e.) (normal hydrogen equivalent).

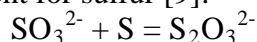
It should also be noted that in practice NiS dissolves in 1M H₂SO₄ (especially when in powder form) with the release of H₂S.

2. Dissolution of NiS in sulfite electrolytes

It is considered promising to use sulfites for dissolving sulfides; autoclave dissolution of sulfides in an aqueous medium by sulfur dioxide was described [8]:



which, however, has a number of drawbacks. It is also known that sulfite - ion is a good solvent for sulfur [9]:



In a saturated Na_2SO_3 solution, intensive dissolution of NiS occurs; moreover, a light green, loose nickel hydroxide is formed, which settles to the bottom of the cell.

Fig. 2 shows the total CVA for Na_2SO_3 concentrations of 250 g/l and 100 g/l. The reverse course of curve (2) in the potential region of 1.8 – 1.4 V is accompanied by periodic current oscillations, indicating the existence of a semiconducting film on the electrode surface [10 - 11], - (possibly NiSO_3), which causes salt passivation.

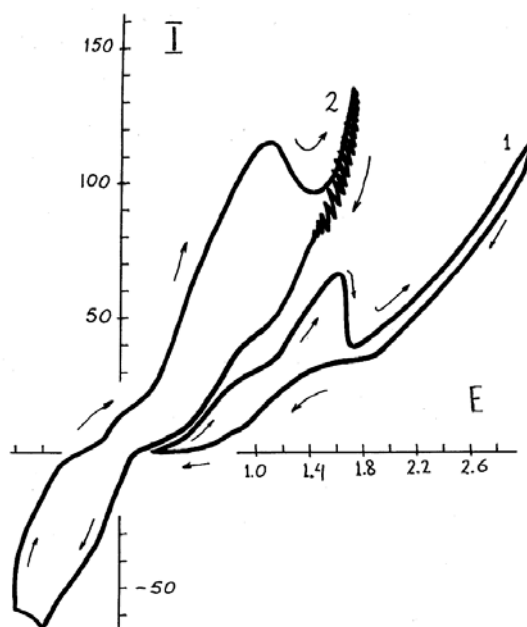


Fig. 2. Cyclic voltammograms of NiS at $90 \pm 0.5^\circ\text{C}$ and Na_2SO_3 content: 1 - 100 g/l; 2 - 250 g/l. E is the electrode potential, V. I is the anode current, mA.

Ammoniac oxidative leaching of sulfide feedstock is widely used in industry [12]. Directly in pure NH_4OH , NiS does not dissolve even with anodic polarization. The introduction of sulfite ion into the ammonia system significantly changes the course of the process. Figure 3 shows two cyclic voltammograms of nickel sulfide in a solution containing 200 g/l Na_2SO_3 and 2% NH_4OH (curve 1) and in a solution containing 100 g/l Na_2SO_3 and 20% NH_4OH .

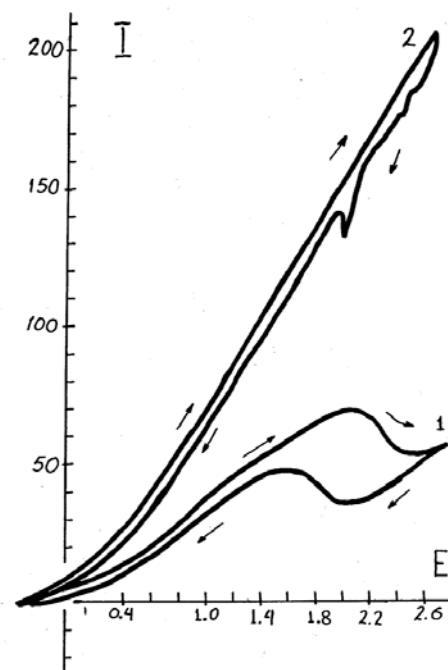


Fig. 3. Cyclic voltammograms of NiS in:

1 – 200 g/l Na_2SO_3 and 2% NH_4OH

2 – 100 g/l Na_2SO_3 and 20% NH_4OH

Temperature: $90 \pm 0,5^\circ\text{C}$, E is the electrode potential, V. I is the anode current, mA.

As can be seen from CVA, the anode branch of curve (1) is accompanied by slight passivation of the electrode, which is apparently of a salt character.

Under the conditions of system (2), the dissolution of NiS proceeds intensively, without passivation. From the surface of the electrode, concentration flows of blue-violet $[\text{Ni}(\text{NH}_3)_n]^{2+}$ are formed, while the surface of nickel sulfide itself remains pure, yellow-gold in color. The reverse course of curve (2) is accompanied by random current fluctuations caused, it seems, by the same reason as in the case of Fig. 2.

3. Behavior of NiS in NH_4OH c $\text{K}_2\text{Cr}_2\text{O}_7$.

The most complete dissolution of nickel sulfide was observed in ammonia solutions. For the preparation of electrolytes, a 10% solution of NH_4OH p.f.a. was used, since it is quite stable at 90°C . In a pure aqueous solution of ammonia, nickel sulfide does not dissolve even with anodic polarization. $\text{K}_2\text{Cr}_2\text{O}_7$ additives lead to excellent dissolution of NiS without passivation - see Fig. 4.

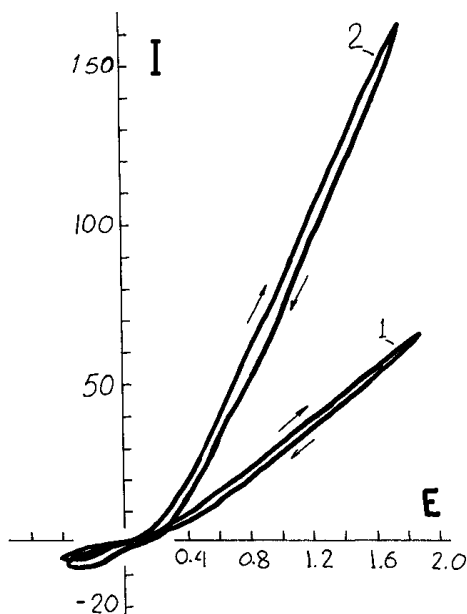
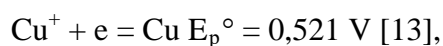


Fig.4. Cyclic voltammograms of NiS in 10 % NH_4OH at $90\pm 0,5^\circ\text{C}$ ($\text{pH} = 12.0$) with additives $\text{K}_2\text{Cr}_2\text{O}_7$: 1 – 6 g/l $\text{K}_2\text{Cr}_2\text{O}_7$; 2 – 30 g/l $\text{K}_2\text{Cr}_2\text{O}_7$. E is the electrode potential, V. I is the anode current, mA.

An increase in the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ only leads to a change in the slope of the potential – current curve. NiS currents practically do not change in time. Sulfur, as in the case of 0.5M $\text{K}_2\text{Cr}_2\text{O}_7$, is not released. The surface of the electrode remains pure white and yellow. With an increase in the ammonia concentration to 25% NH_4OH , the solution was boiled at $58\text{--}60^\circ\text{C}$ and the nickel sulfide surface cracked, possibly similar to the corrosion cracking of brass in aqueous ammonia solutions observed by the authors.

4. Behavior of NiS in copper ammine

There is still no consensus on the catalytic effect of copper. It is believed [3] that copper can stand out on the surface of sulfides in an elementary form, forming microvoltaic pairs that enhance the anode potential in individual sections of sulfide. On the other hand, Cu^{2+} ions present in an acidic solution can act as an additional oxidizing agent:



capable to oxidize sulfide sulfur to elemental. Perhaps it is copper that prevents the further oxidation of elemental sulfur to a sulfate ion, which is extremely convenient for technological reasons: sulfide sulfur is removed from the process in the form of elemental sulfur.

Unfortunately, the process of anodic dissolution of nickel sulfides in acidic copper sulfate electrolytes is rapidly inhibited due to the formation of a passivating Cu_2S film on the surface of nickel sulfide.

The appearance of copper ions in an ammonia solution leads to a virtually non-passivation anodic dissolution of nickel sulfide (Fig. 5), and stationary currents behave stably, and an increase in copper concentration leads to an increase in the process speed (Fig. 6).

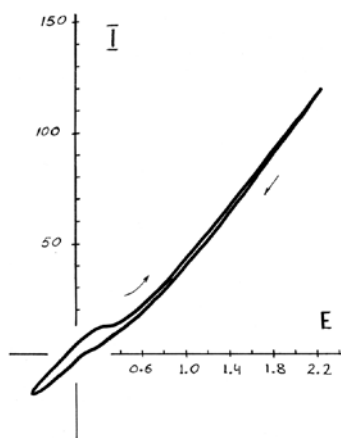


Fig. 5. CVA NiS – at $60\pm 0.5^\circ\text{C}$ in: $0.5\text{M } [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ in $25\% \text{NH}_4\text{OH}$
I is the anode current, mA. E is the electrode potential, V (n.h.e).

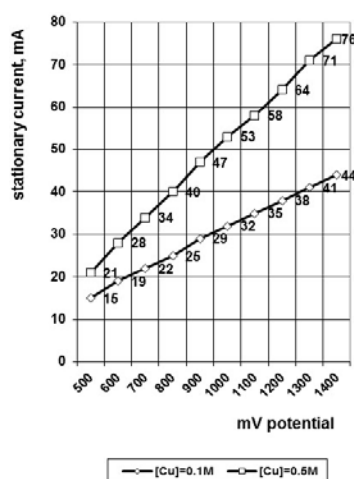


Fig. 6. Behavior of NiS (50%) in $25\% \text{NH}_4\text{OH}$ c $[\text{Cu}(\text{NH}_3)_2]\cdot\text{SO}_4$ at $60\pm 0,5^\circ\text{C}$.

RESULTS AND DISCUSSION

Although at present most hydrometallurgical industries are focused on acidic nickel sulfide processing schemes, the positive results obtained by studying the anodic dissolution of NiS in ammonium sulfite, ammonium bichromate, and copper-ammonia media open up the possibility of developing new technologies using these media, which becomes especially relevant with increasing environmental requirements and the need for processing of poor and substandard raw materials.

CONCLUSION

1. Potassium bichromate and copper (II) complexes have an oxidation-depassivating effect on the anodic dissolution of NiS in NH_4OH .

2. The slope angle of the Tafel right of nickel sulfide dissolution increases with increasing content of potassium dichromate and copper (II) complexes.
3. When NiS is dissolved in the presence of $K_2Cr_2O_7$, sulfide sulfur is oxidized to SO_4^{2-} .
4. In a pure Na_2SO_3 solution, intensive dissolution of NiS occurs, accompanied by the formation of insoluble hydroxyl compounds Ni^{2+} , the composition of which varies with change of pH.
5. The combined action of NH_4OH and Na_2SO_3 causes intensive dissolution of NiS with the formation of ammonia complexes $[Ni(NH_3)_n]^{2+}$.

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